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14. ABSTRACT Recent developments in the study of microbiologically influenced corrosion (MIC) represent major shifts in the identification of mechanisms and our understanding of MIC. Mechanisms cannot be deduced by the identification of specific microorganisms. Instead it is necessary to understand the chemistries produced by those microorganisms. For example, iron-oxidizing bacteria (IOB) and sulfate-reducing bacteria (SRB) are routinely identified as groups of microorganisms that influence corrosion. IOB are known to cause under deposit corrosion in some materials. The ability of SRB to produce corrosive hydrogen sulfide from the reduction of sulfate, sulfite, thiosulfate and elemental sulfur is well documented. However, both groups of microorganisms can produce other chemistries that are corrosive. Furthermore there is now recognition that global observations of MIC-related phenomena, e.g., ennoblement of passive alloys, can be due to site-specific mechanisms. Multiple mechanisms can be used to rationalize global observations of ennoblement in fresh water, estuarine and marine environments, but the mechanism for ennoblement at a particular location may be site-specific.					
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Recent developments in the identification of mechanisms for microbiologically influenced corrosion

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ABSTRACT

Recent developments in the study of microbiologically influenced corrosion (MIC) represent major shifts in the identification of mechanisms and our understanding of MIC. Mechanisms cannot be deduced by the identification of specific microorganisms. Instead it is necessary to understand the chemistries produced by those microorganisms. For example, iron-oxidizing bacteria (IOB) and sulfate-reducing bacteria (SRB) are routinely identified as groups of microorganisms that influence corrosion. IOB are known to cause under deposit corrosion in some materials. The ability of SRB to produce corrosive hydrogen sulfide from the reduction of sulfate, sulfite, thiosulfate and elemental sulfur is well documented. However, both groups of microorganisms can produce other chemistries that are corrosive. Furthermore there is now recognition that global observations of MIC-related phenomena, e.g., ennoblement of passive alloys, can be due to site-specific mechanisms. Multiple mechanisms can be used to rationalize global observations of ennoblement in fresh water, estuarine and marine environments, but the mechanism for ennoblement at a particular location may be site-specific.

Keywords: MIC, mechanisms, IOB, SRB, ennoblement

IRON-OXIDIZING BACTERIA

Iron-oxidizing bacteria (IOB) derive energy from the oxidation of ferrous (Fe^{2+}) to ferric (Fe^{3+}) at/near neutral pH and in some cases the result is the formation of dense tubercles or rusticles of filamentous Fe oxides. At pH >5, Fe^{2+} spontaneously oxidizes to Fe^{3+} ($t_{1/2}$ <15 minutes). At circumneutral pH IOB compete with abiotic Fe^{2+} oxidation in low O_2 environments. IOB have been implicated in MIC since the 1960's.¹ It is well established that tubercle formation by IOB produces an O_2 concentration cell. Most of the documented MIC case histories associated with IOB tubercle formation have involved exposure of austenitic 300 series (304 or 316) stainless steel in untreated well water (200-300 ppm $[\text{Cl}^-]$) and chlorinated drinking water.²⁻⁷ IOB form dense deposits, excluding O_2 from the area immediately under the deposit. In an oxygenated environment, the area

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deprived of O_2 becomes a relatively small anode compared to the large surrounding oxygenated cathode. Metal is oxidized at the anode and pH decreases. The extent of the decrease is determined by the alloy composition.⁸ For this reason, O_2 concentration cells produce particularly aggressive corrosion on 300 series stainless steels, containing 17.5 to 20% Cr. Cl^- migrates from the electrolyte to the anode to neutralize charge, forming heavy metal chlorides that are extremely corrosive. Under these circumstances, pitting involves the conventional features of differential aeration, a large cathode-to-anode surface area and the development of acidity and metallic chlorides. The mechanism for MIC is determined by the microorganisms (IOB), the nature of the electrolyte (Cl^-) and the composition of the substratum (300 series stainless steel).

Recently IOB were identified in corrosion products on carbon steel pilings in a fresh water lake.⁹ Corrosion of carbon steel in this situation cannot be due to the previously-described, well-characterized mechanism for IOB influenced corrosion of 300 stainless steels. Oxygen concentration cells alone cannot drive aggressive corrosion of carbon steel and the electrolyte contains approximately 10-20 parts-per-million Cl^- . Instead, Ray *et al.*⁹ demonstrated that stalk-forming, IOB colonized the carbon steel sheet pilings and produced tubercles, made up of intact and/or partly degraded remains of bacterial cells mixed with amorphous hydrous ferric oxides. The reducing conditions beneath the tubercles caused copper, dissolved in the water, to precipitate. A galvanic couple was established between the copper layer and the iron substratum. The result was aggressive localized corrosion. The mechanism for corrosion depended on the dense deposits produced by the IOB, the copper-containing electrolyte and the material vulnerability (galvanic corrosion of carbon steel in contact with copper). Accelerated corrosion of carbon steel in contact with copper in fresh water has been acknowledged since the early 1920's.¹⁰ The individual events leading to the corrosion of carbon steel pilings in fresh water are predictable, i.e., colonization of the surface by IOB followed by the establishment of differential aeration cells. However, this was the first report of deposition of copper due to localized lowering of potential due to the activities of microorganisms and the influence of the resulting galvanic cell on corrosion of carbon steel.

There are other ways in which IOB could potentially influence corrosion. The presence of IOB generated stalks in biofilms may provide a reactive mineral structure to which other bacteria adhere, and thus potentially increase overall bacterial interaction with the corrosion products and steel surface. Bacteriogenic iron oxides formed in response to chemical or bacterial oxidation of Fe^{2+} to Fe^{3+} have reactive surfaces and act as sorbents of dissolved metal ions. Enrichments of Pb, Cd, Al, Cu, Cr, Mn, Sr and Zn have been reported.¹¹⁻¹⁴ Several investigators have reported metal-binding, including Cu, by bacterial exopolymers.¹³ The stalk material produced by IOB is thought to contain a polysaccharide; however its composition has not been elucidated. Additionally, bacteriogenic iron oxides are readily reduced by other bacteria, e.g., Fe^{3+} -reducing bacteria and SRB in comparison with synthetic iron oxides leading to enhanced growth of anaerobic colonizers.

Sulfate-reducing bacteria

The ability of sulfate reducing bacteria (SRB) to produce corrosive sulfide from the reduction of sulfate, sulfite, thiosulfate and elemental sulfur is well documented, particularly in the petroleum industry. These organisms are found in every anaerobic habitat examined to date and their population numbers are routinely monitored as part of pipeline integrity management efforts. SRB are a diverse group of bacteria that can ferment both organic and inorganic compounds, using a wide variety of electron donors and acceptors. In the absence of an electron acceptor, SRB can enter into syntrophic relationships with methanogens or other H_2 -consuming organisms. The diversity of sulfate reducing prokaryotes found in oil reservoirs has been reviewed.¹⁵ These organisms fall into two general groups - those that completely oxidize their organic substrates and produce CO_2 as an endproduct, and those that incompletely metabolize their substrates and produce acetate as well as CO_2 . The complete oxidizers are able to utilize a wide variety of substrates including *n*-alkanes.¹⁶

Carbon dioxide (CO_2) corrosion was described in the 1940's.¹⁷ Since that time the corrosion of carbon steel due to the presence of CO_2 in oilfield brines has received considerable attention. Through the 1970's the major mechanisms attributed to CO_2 corrosion were erosion corrosion, uniform corrosion and acidity due to CO_2 in the water in the form of carbonic acid. Crolet and Bonis¹⁸ concluded that the key determinate of CO_2 corrosion was the chemical composition of the produced water. "Indeed this modulates all the possible effects of the dissolution of CO_2 into

water." For example, under high CO₂ pressures they reported that the pH of produced waters depended as much on the physical chemistry of water as on the partial pressure of the acidifying gas and identified bicarbonate, acetate and calcium as important for the evolution of pH as a function of CO₂ partial pressure. They suggested that in the presence of H₂S, additional species must be considered. The impact of "carbon dioxide corrosion" in oil and gas pipelines has been recently reviewed.¹⁹ One of the conclusions of that article is that the electrochemistry of mild steel dissolution in CO₂ solutions is largely understood, but outstanding issues relating to the impact of other chemical components, in particular H₂S and acetic acid, still need a more fundamental understanding. The exacerbation of carbon dioxide corrosion of carbon steel in the presence of acetate is a well-known phenomenon in the oil industry. Acetate is a common constituent of reservoir fluids and several hypotheses for the abiogenic origin have been advanced.²⁰ These include the interaction of oil and water, oxidation of suitable acid precursors and the pyrolytic destruction of kerogen or oil components.

Suffita *et al.*²¹ contend that fermentative bacteria, acetogenic bacteria and SRB residing in pipeline facilities can influence corrosion through the production of CO₂ and acetate under the prevailing anaerobic conditions. The authors suggest that it is reasonable to expect the same type of mutualistic bacterial associations to also occur in facilities used for hydrocarbon extraction, processing, and transport. In these facilities, complex forms of organic matter including hydrocarbons are broken down into simpler components and eventually into lower molecular weight fatty acids and alcohols. These components, in turn, are converted to acetate, hydrogen, and carbon dioxide by syntrophic bacteria that rely on the removal of acetate and hydrogen by other organisms to render the energetics of such bioconversions favorable. Many pathways of anaerobic metabolism converge on acetate. Bacterial syntrophism can be based on interspecies acetate utilization as well as hydrogen consumption.^{22,23} Carbon dioxide is the ultimate mineralized endproduct resulting from the microbial degradation of the myriad forms of polysaccharides, proteins, nucleic acids, and lipids in any environment. Geological evidence suggests that hydrocarbons must be included in this list of biodegradable forms of organic matter.²⁴ In fact, the susceptibility of various hydrocarbons to anaerobic biodegradation is well known and the subject has been reviewed repeatedly over the last decade.²⁵⁻³³ Oxidation of many different types of hydrocarbons can be coupled with the reduction of a variety of electron acceptors other than oxygen with CO₂ as the resulting endproduct. Anaerobes can couple their metabolism in syntrophic associations that ultimately allow for the conversion of the petroleum components to the other major mineralized endproduct – methane.³⁴⁻³⁸

The pKa of acetic acid/acetate in oil brines is near 4.7.³⁹ A small fraction (~ 1%) of the ion will persist as the protonated acid in the bulk aqueous phase at normal pipeline pH values of ~ 6.7, whereas 10% may be protonated in some locales associated with solids near pits. Protonated acetic acid contributes to corrosiveness of the aqueous fluids as well as decreasing the aqueous phase pH to a lower level, shifting more of the bicarbonate pool to CO₂ where the pKa for CO₂ is ~ 6.35 and 3.85 for H₂CO₃.

A potential source of CO₂ production within pipelines is acid producing bacteria (APB). As bacteria oxidize organics to volatile fatty acids up to a mole of CO₂ can be released per mole of volatile fatty acid produced. When acetic acid is formed by APB it can result in low pH in the vicinity of the pits and precipitation of ferric iron. Within a pit where ferric iron precipitates the local pH may be less than 3.0. Assuming a CO₂ partial pressure of ~ 1 atm (similar to twice that of the bulk aqueous phase) and acetate concentration similar to the bulk phase of 100-1000 ppm then an expected propagation of corrosion within a pit may be > 2 mm/yr in 3% NaCl. Production of 1.2-1.8 moles of CO₂ from the oxidation of organics could be expected per mole of sulfate reduced. For example, reduction of 160mg/L sulfate (1.7 mM) would result in at least 2 mM CO₂. Since 100% of a gas phase is ~42mM at 135° then 2mM of CO₂ could correspond to an addition of 4.5% or more of CO₂ into the pipelines.

Extrapolating from Garsany *et al.*³⁹ and Hedges and Mc Viegh⁴⁰ one appreciates a potential interplay between CO₂, acetate and pH with corrosion in bulk phase fluids and perhaps in pit locales. One could hypothesize that combining CO₂ contributions from reservoir fluids plus SRB and APB the pCO₂ could approach 5-15 psi pCO₂, values that according to NACE (SPO106-2006 App. C)⁴¹ "may be corrosive in the presence of water." Considering the mildly acidic pH with less than 0.5% salinity in the presence of 100-1000 ppm of acetate/acetic acid contributions the bulk phase fluids could approach the mid point of the range that "may be corrosive in presence of water." When considering localities associated with pits where more acid pH, likely production of acetic acid

and a higher contribution of protonated acetic acid they may be representative of the “double whammy” described by Hedges and McVeigh.⁴⁰

ENNOBLEMENT

Ennoblement of the open circuit potential (E_{corr}) of passive alloys, a shift in the positive direction, as a result of biofilm formation is a global phenomenon and has been reported in fresh, brackish and seawaters.⁴² Theoretically, E_{corr} ennoblement should increase the probability for pitting and crevice corrosion initiation and propagation of some passive alloys, particularly those alloys for which the pitting potential is close to E_{corr} . Numerous researchers have shown that increased cathodic reduction rates accompany ennoblement of E_{corr} . However, attempts to relate ennoblement to a single microbiologically mediated mechanism have failed.⁴³⁻⁴⁶

Comparison of ennoblement data from different locations and different investigators is complicated because extent of ennoblement is affected by sample size, flow rate and temperature. Ennoblement has been measured for metals boldly exposed, metals incorporated in crevice assemblies and polarized metals. The alloys tested include, but are not limited to: UNS S30400, S30403, S31600, S31603, S31703, S31803, N08904, N08367, S44660, S20910, S44735, N10276, N06625, platinum, gold, palladium, chromium, titanium, and nickel.

In fresh water, ennoblement can be the result of microbial deposition of manganese and localized corrosion has been related directly to the biomineralized deposits on the surface of 300 series stainless steels.⁴⁷⁻⁴⁹ Dexter *et al.*⁵⁰ reported that manganese was found within biofilms on Nitronic 50 (UNS S20910) coupons exposed in Delaware Bay. Delaware Bay is an estuary, strongly influenced by the Delaware River. Water at this location has been referred to as both marine and coastal seawater.^{50,51} Salinity varies from 26 to 33 ppt and the temperature from 20 to 28 °C. Manganese distribution maps prepared by the U.S. Geological survey data⁵² indicate that manganese concentration in the Delaware River basin is high. Therefore, E_{corr} ennoblement in Delaware Bay may be due to microbial manganese deposition and the data generated at that site may have little in common with data collected from other coastal locations. Manganese is not routinely reported in marine biofilms associated with ennoblement.

Martin *et al.*⁵³ compared ennoblement of several alloys at two coastal seawater locations – Key West, Florida and Delaware Bay (Figures 1a & 1b). The two locations have different temperatures and different salinities. Martin *et al.*⁵³ demonstrated that E_{corr} ennoblement is site specific, varying 100 mV vs. saturated calomel electrode (SCE) between locations, with higher potentials at Delaware Bay. Localized corrosion was observed for alloy SS3040 exposed in Key West, but not in Delaware Bay.

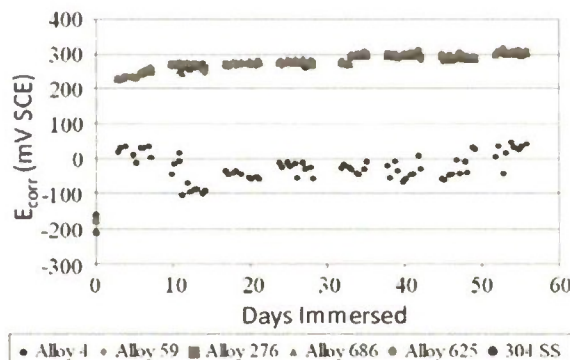


Figure 1a. E_{corr} of Ni-Cr-Mo alloys and 304SS during 60-day exposure at Key West, showing corrosion potential ennoblement approaching 300 mV SCE in the first 30.⁵³

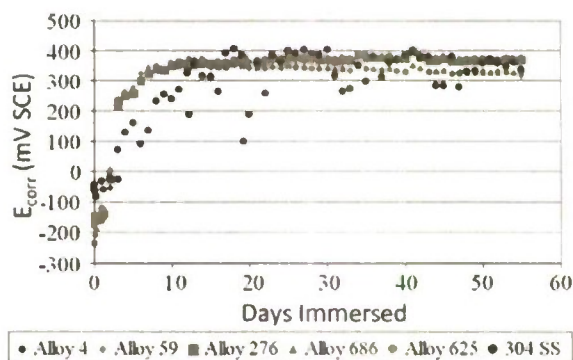


Figure 1b. E_{corr} of Ni-Cr-Mo alloys and 304SS during 60-day exposure at Delaware Bay, showing corrosion potential ennoblement approaching 300 mV SCE in the first 7 days.⁵³

Several mechanistic explanations have been proposed for ennoblement in marine waters. Little and Mansfeld⁵⁴ categorized the proposed mechanisms into three categories: thermodynamic, kinetic, and alteration of the nature of the reduction reaction itself. Thermodynamic arguments for ennoblement suggest that either a pH decrease at the metal/biofilm interface or a local increase of the partial pressure of oxygen ($p\text{O}_2$) raises the reversible potential of the oxygen electrode

($E^0_{O_2}$) (Figure 2). For aerobic biofilms, changes in $E^0_{O_2}$ due to changes in pO_2 would be small. For seawater, a decrease of local pH from 8 to 3 would account for an ennoblement of about 300 mV, assuming that the exchange current density for the oxygen reduction reaction ($i^0_{O_2}$) and the cathodic Tafel slope remain constant (Figure 2) where the initial E^1_{corr} changes to E^2_{corr} as $E^{0.1}_{O_2}$ increases to $E^{0.2}_{O_2}$.

Kinetic arguments for ennoblement suggest that the rate of oxygen reduction at a given potential (E) can also increase due to an increase of $i^0_{O_2}$ leading to an increase of E^1_{corr} to E^3_{corr} (Figure 2).⁵⁴ Dexter and Gao⁵⁵ suggested that increased oxygen reduction rates might be due to an increase of $i^0_{O_2}$, mediated by biopolymer metal complexes known to catalyze oxygen reduction. The nature of these organometallic catalysts has been the topic of wide discussion. Johnsen and Bardal⁵⁶ observed that the presence of a biofilm dramatically increased the current density required to polarize stainless steel to a potential of -400 mV (SCE), adequate to provide cathodic protection in seawater. They attributed this increase to a lack of calcareous deposits and an enhanced organometallic catalysis of the oxygen reduction reaction beneath the biofilm. The mechanism of organometallic catalysis has been criticized, however, because ennoblement is also observed on more noble metals, including titanium and platinum, which lack transition elements thought to be necessary to form catalyzing complexes.⁵⁷ The nature of the passive layer has also been suggested to play a role in ennoblement by altering the reduction rate of oxygen.⁵⁸ Differences in the semiconductive properties of the passive film have also been suggested to affect an alloys susceptibility to ennoblement.⁵⁹

In the previous discussion it was assumed that microorganisms change the rate of the cathodic reaction and for neutral, aerated solutions, the cathodic reaction is reduction of oxygen. It is possible that microorganisms change the rate-determining step in an electrochemical reaction or produce an entirely different mechanism. Chandrasekaran and Dexter⁶⁰ suggested that reduction in surface pH and production of hydrogen peroxide (H_2O_2) at low oxygen concentration are important contributory factors for ennoblement. The contribution of H_2O_2 to ennoblement is related to its relatively noble thermodynamic potential at low pH. Theoretically, at pH = 2.9 and pO_2 = 0.5 ppm, the presence of 8.2 mM H_2O_2 would produce an increase in the reversible potential of 0.5 V. These specific conditions have not been measured in an actual biofilm. Chandrasekaran and Dexter⁶⁰ measured H_2O_2 concentrations ranging from 1.3 to 6.6 mM in biofilms on platinum coupons after a 1-year exposure. Feron *et al.*⁶¹ and Dupont *et al.*⁶² observed ennoblement of stainless steels exposed in "biochemical artificial seawater," artificial seawater amended with glucose and glucose oxidase. The enzyme catalyzes the oxidation of glucose to gluconic acid and H_2O .⁶³ Washizu *et al.*⁶⁴ examined the role of H_2O_2 in ennobling biofilms by addition of catalase and peroxidase, enzymes known to decompose H_2O_2 . Concentrations of 10-30 ppm H_2O_2 were identified in natural biofilms that produced ennobled E_{corr} values. Addition of catalase or peroxidase to the bulk solution decreased H_2O_2 concentrations to below 0.5 ppm and ennoblement was decreased resulting in E_{corr} values observed in sterile conditions.

Theoretically it is also possible that E_{corr} becomes ennobled due to a decrease of passive current density (i_p) at constant $E^0_{O_2}$, $i^0_{O_2}$, and Tafel slope, leading to a change from E^1_{corr} to E^4_{corr} (Figure 2). Eashwar *et al.*⁶⁵ proposed a mechanism in which siderophores (iron chelators) produced by microorganisms within biofilms at neutral pH act as inhibitors and enhance passivity of the stainless steel by reducing i_p (Figure 2). Siderophores, produced by all microorganisms, have been shown to possess excellent corrosion inhibition properties.⁶⁶ Eashwar *et al.*⁶⁵ called the theory "imaginary, but ... based on careful analysis of both the literature on ennoblement and ecological factors inherent in marine biofilms."

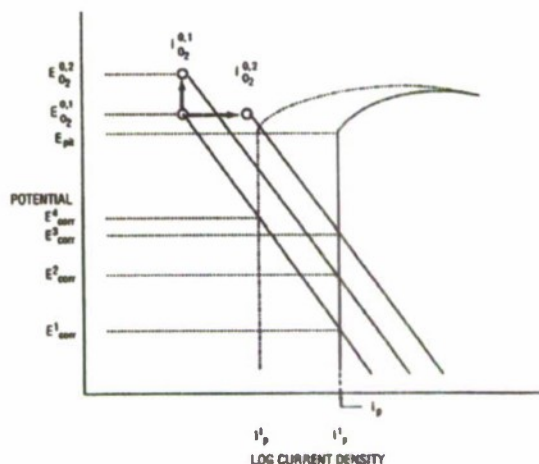


Figure 2. Schematic polarization curves for stainless steel in seawater.⁵⁴

CONCLUSIONS

Understanding MIC mechanisms requires more than the identification of specific groups of microorganisms. IOB and SRB can influence corrosion via multiple mechanisms. It has been reported in locations worldwide that ennoblement produced by natural biofilms increases the probability of pit and crevice initiation on a variety of passive alloys, as well as the rate of localized corrosion propagation. However, observations of ennobled E_{corr} alone cannot be used to predict an increased likelihood of localized corrosion for a crevice corrosion prone alloy. Multiple mechanisms can be used to rationalize global observations of ennoblement in fresh water, estuarine and marine environments, but the mechanism for ennoblement at a particular location may be site-specific.

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